Direct Synthesis of Styrene by Rhodium-Catalyzed Oxidative Arylation of Ethylene with Benzene

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Various rhodium complexes were examined for oxidative arylation of ethylene with benzene to directly produce styrene. Using $Rh(ppy)_2(OAc)$ (**1**) (ppyH = 2-phenylpyridine), the reaction of benzene with ethylene gives styrene and vinyl acetate in 77 and 23% selectivities, respectively, in contrast to the selectivities using $Pd(OAc)_2$, which are 47% styrene and 53% vinyl acetate. The observation that complex **1** is an active catalyst for both styrene formation and H–D exchange between CH_3CO_2D and C_6H_6 suggests that styrene formation involves a Rh-mediated, benzene CH bond activation process. The crystal structures of complex **1** and $Rh(ppy)_2(acac–O,O')$ (**2**) (acac = acetylacetonato) are also reported. $Rh(acac)(CO)_2$ also works as catalyst for styrene formation by addition of acacH and O_2 without any oxidizing agent, such as Cu salt. In this system, vinyl acetate is not formed at all in spite of the presence of acetic acid.   © 2002 Elsevier Science (USA)

Key Words: rhodium complex; oxidative arylation; homogeneous catalysis; CH bond activation; crystal structure.

1. INTRODUCTION

Derivatives from aromatic compounds such as alkylbenzene, phenol, aniline, and naphthalene are large-quantity chemicals manufactured by chemical industries. Especially, styrene is a major derivative from benzene. The current industrialized process for producing styrene consists of two parts: the alkylation of benzene with ethylene to form ethylbenzene and the dehydrogenation of ethylbenzene to form styrene. Therefore, the ability to directly form styrene from benzene and ethylene using aromatic C–H bond activation leading to C–C bond formation is considerably attractive from the industrial point of view.

Numerous efforts related to homogeneous C–H bond activation of aromatic compounds by discrete transition metal complexes through various mechanisms have been reported (1–15). Group VIII metal complexes can also be employed for olefin oxidation reactions such as Pd-catalyzed partial oxidation of ethylene, as is done in the well-known Wacker reaction for forming acetaldehyde (16, 17) and in oxidative vinylation of acetic acid to produce vinyl acetate (18). Fujiwara *et al.* and others have reported significant work in attempting direct formation of styrene by oxidative arylation of ethylene catalyzed by Pd complexes combining arene activation with oxidation (19, 20). Hong and Yamazaki have reported direct formation of styrene by another approach, using a Rh(0) complex, where 3-pentanone is simultaneously produced, and the mechanism is completely different from that of Fujiwara *et al.* (21). Although Pd-catalyzed oxidative arylation of ethylene has already been developed, the reaction catalyzed by rhodium complexes has not been well investigated.

We recently reported on Rh-catalyzed oxidative arylation of ethylene with benzene to produce styrene with higher selectivity than that of vinyl acetate (22, 23). Further details regarding the reaction mechanism and the scope of catalyst systems are described below.

2. EXPERIMENTAL

2.1. General

GC analyses were performed with a Shimadzu GC-17A gas chromatography equipped with a flame ionization detector (FID) and a crosslinked methyl silicone gum capillary column, PONA. GC–MS analyses were performed with a Hewlett Packard HP5971A GC–MS system equipped with a crosslinked methyl silicone gum capillary column, PONA. ^1H NMR spectra were recorded on JEOL EX-400 (400 MHz) and Bruker ARX300 (300 MHz) instruments. ^{13}C NMR spectra were recorded on a JEOL EX-400 (100 MHz) instrument with complete proton decoupling. FD mass spectra were measured on a JEOL AX505 instrument. Elemental analyses were performed at the Analytical Group, Central Technical Research Laboratory, Nippon Mitsubishi Oil Corporation. Single-crystal X-ray diffraction analyses were measured at Mitsui Chemicals Analytical

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Center, Inc. The product yields were determined by GC (FID) analyses using chlorobenzene as an internal standard that was introduced into the reaction solution after the reaction. The retention times of products were confirmed by standards. Products were also qualitatively determined by GC–MS analyses. The compounds that act as GC standards for retention time are commercially available. [Rh(bzq)$_2$Cl]$_2$, [Ir(ppy)$_2$Cl]$_2$ (24), RhCp*Cl(acac–O,O′), [RhCp*(μ-acac–O,O′,C^3)]$_2$(BF$_4$)$_2$, Ir(Cp*)(acac–O,O′)Cl, Ir(Cp*) (acac–O,O′)(acac–C^3) (25), and [Ir(μ-acac–O,O′,C^3)(acac–O,O′)(acac–C^3)]$_2$ (26) were prepared as reported in the literature. [Rh(ppy)$_2$Cl]$_2$, [RhCp*Cl$_2$]$_2$, [Ir(Cp*)Cl$_2$]$_2$, and [Rh(NBD)(DPPB)](BF$_4$) were purchased from Aldrich Chemical Co. Rh(acac)(CO)$_2$ was purchased from Strem Chemicals, Inc. PhHg(OAc) was purchased from Alfa Aesar.

Since oxygen is introduced into the reaction system, it is important to be aware of explosion limits. The explosion limits for the oxygen lean side of an oxygen/ethylene mixture is 20% oxygen, and for the oxygen rich side is 97% oxygen. However, including a margin of vapor pressure of benzene at our reaction condition, the explosion limits for the oxygen lean side of an oxygen/(ethylene + benzene) mixture, in which ethylene/benzene is 1/1, is 28% oxygen. According to the above information, ethylene and oxygen measured into the reactor will be outside the explosive region. Concerning, H–D exchange experiments in which no ethylene is added, methane, which is an inert gas for the reaction, is added to the reactor as a diluent hydrocarbon to the benzene gas phase, lowering the partial pressure of the oxygen to the oxygen lean side of the explosion limits.

2.2. Oxidative Olefin Arylation

The typical reaction procedure is as follows (Table 1, entry 2). A 10-ml stainless steel autoclave equipped with a glass insert and a magnetic stir bar was charged with 27.2 mg of Cu(OAc)$_2$ and 3 ml of a benzene/acetic acid solution of complex **1** which contained 1.0 mM complex **1** and 10.6 M benzene. The reactor was degassed with N$_2$, pressurized with 1.55 MPa of ethylene, sequentially pressurized with O$_2$ up to 2.10 MPa, and heated to 180°C with stirring for 20 min. The liquid phase was analyzed by GC (FID) and GC–MS at the end of the reaction. All other oxidative arylation reactions were performed using similar procedures.

Regarding Table 1, entry 27, a catalyst/benzene/acetic acid/acacH solution which contained 1.0 mM Rh(acac)(CO)$_2$, 10.6 M benzene, and 0.67 M acacH was applied for the reaction.

2.3. H–D Exchange

The reaction was monitored by measuring the mass profile for benzene using GC–MS for deuterium incorporation into the starting C$_6$H$_6$. The mass range from 78 to 84 was examined for each reaction. The molar ratio of iso-topes was obtained by calculation to deconvolute the fragments from each parent. In Table 2, entry 35, a 10-ml stainless autoclave equipped with a glass insert and a magnetic stir bar was charged with 27.2 mg of Cu(OAc)$_2$, 3 ml of a benzene/CH$_3$CO$_2$D solution (6.0 M benzene), and 1.1 mg of complex **1**. The reactor was degassed with methane, pressurized with 1.55 MPa of methane, sequentially pressurized with O$_2$ up to 2.10 MPa, and heated to 180°C with stirring for 20 min. The liquid phase was sampled and analyzed by GC–MS at the end of the reaction. Other H–D exchange reactions were performed using the same procedure as above.

2.4. Synthesis of Complex **1**

A solution of [Rh(ppy)$_2$Cl]$_2$ (500 mg, 0.560 mmol) in benzene (30 ml) was mixed with a solution of KOAc (330 mg, 3.36 mmol) in ethanol and refluxed for 3 h, whereupon KCl gradually formed as a white precipitate. The solution was filtered to remove KCl and the filtrate was evaporated to dryness to yield a yellow residue. H$_2$O (70 ml) was added to the residue, stirred, and filtered to obtain a yellow product, which was washed with H$_2$O and then dried under vacuum overnight. Yellow prismatic crystals were obtained by diethylether vapor diffusion into a CH$_2$Cl$_2$ solution of the isolated compound in a refrigerator. The yield was 86% (453 mg). ^{1}H NMR (400 MHz, δ, CDCl$_3$): 2.03 (s, 3H, CH$_3$), 6.15 (d, 2H, ppy), 6.74 (t, 2H, ppy), 6.88 (t, 2H, ppy), 7.30 (m, 2H, ppy), 7.56 (d, 2H, ppy), 7.89 (m, 4H, ppy), 8.89 (d, 2H, ppy). ^{13}C NMR (101 MHz, δ, CDCl$_3$): 24.6 (O$_2$CCH$_3$), 118.7, 122.1, 122.3, 123.8, 129.1, 133.7, 137.4, 143.8, 149.9, 164.8 (ppy), 164.7 (J$_{Rh–C}$ = 36.8 Hz, ppy), 186.0 (O$_2$CCH$_3$). FDMS: 470 (M$^+$). Analysis calculated for C$_{24}$H$_{19}$N$_2$O$_2$Rh: C, 61.29; H, 4.07; N, 5.96. Found: C, 60.90; H, 4.35; N, 5.94.

2.5. Synthesis of Complex **2**

A solution of [Rh(ppy)$_2$Cl]$_2$ (500 mg, 0.560 mmol) in benzene (30 ml) was mixed with a solution of Kacac (460 mg, 3.33 mmol) in ethanol (12 ml) and refluxed for 3 h. In the course of the reaction, a pale yellow precipitate formed. The precipitate was collected on a filter and washed with ethanol. H$_2$O (70 ml) was added to the obtained solid. After the slurry was stirred to dissolve KCl, it was filtered, washed with H$_2$O, and dried under vacuum overnight to obtain a yellow product. Yellow plate crystals were obtained by diethylether vapor diffusion into a CH$_2$Cl$_2$ solution of the isolated compound in a refrigerator. The yield was 68% (387 mg). ^{1}H NMR (400 MHz, δ, CDCl$_3$): 1.87 (s, 6H, acac CH$_3$), 5.22 (s, 1H, acac CH), 6.28 (d, 2H, ppy), 6.77 (t, 2H, ppy), 6.89 (t, 2H, ppy), 7.20 (m, 2H, ppy), 7.59 (d, 2H, ppy), 7.84 (m, 4H, ppy), 8.49 (d, 2H, ppy). FDMS: 510 (M$^+$). Analysis calculated for C$_{27}$H$_{23}$N$_2$O$_2$Rh: C, 63.54; H, 4.54; N, 5.49. Found: C, 63.25; H, 4.49; N, 5.46.

2.6. Collection and Reduction of X-Ray Data

Crystals of complexes **1** and **2** were subjected to single-crystal X-ray diffraction analysis. Unit cell parameters for **1** were obtained from a least-squares refinement of 25 reflections in the range $29.31° < 2\theta < 29.84°$. Unit cell parameters for **2** were obtained from a least-squares refinement of 25 reflections in the range $30.27° < 2\theta < 33.82°$. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo $K\alpha$ radiation and a rotating anode generator. A linear correction factor was applied. The Lorentz polarization correction was made to the collected data.

2.7. Solution and Refinement of the Structure

The structures of **1** and **2** were solved by and expanded using Fourier techniques (DIRDIF94 (27)). The nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included, but their positions were not refined. The final cycle of full-matrix least-squares refinement of **1** on F was based on observed reflections and converged with unweighted and weighted agreement factors ($R = \sum ||Fo| - |Fc||/ \sum |Fo|$ and $Rw = [\sum w(|Fo|-|Fc|)^2/ \sum w|Fo|^2]^{1/2}$). The final cycle of full-matrix least-squares refinement of **2** on F^2 was based on observed reflections and converged with unweighted and weighted agreement factors ($R = \sum ||Fo| - |Fc||/ \sum |Fo|$ and $Rw = [\sum w(|Fo|^2 - |Fc|^2)^2/ \sum w(|Fo|^2)^2]^{1/2}$). All calculations were performed using the TeXsan (28) crystallographic software package. ORTEP images were drawn by the Ortep-3 for Windows (29) software.

3. RESULTS AND DISCUSSION

3.1. Oxidative Arylation of Ethylene with Benzene to Produce Styrene

Table 1 shows the comparison study of catalysts for the reaction of benzene with ethylene in a benzene/AcOH solution under various conditions. First, we examined the activities of [Rh(ppy)$_2$Cl]$_2$ (ppyH = 2-phenylpyridine), Rh(ppy)$_2$(OAc) (**1**) (OAc = acetate), and Rh(ppy)$_2$(acac–O,O$'$) (**2**) (acac = acetylacetonato), which have, respectively, an anionic ligand as a leaving group to make an active site and two rigid chelate ppy ligands functioning as translabilizing groups, for oxidative arylation of ethylene with benzene in the presence of O$_2$ and Cu(OAc)$_2$, as shown in Scheme 1. Rh complexes having ppy ligands have been well documented regarding spectroscopic property and electrochemistry (30, 31), whereas the catalysis of the complexes
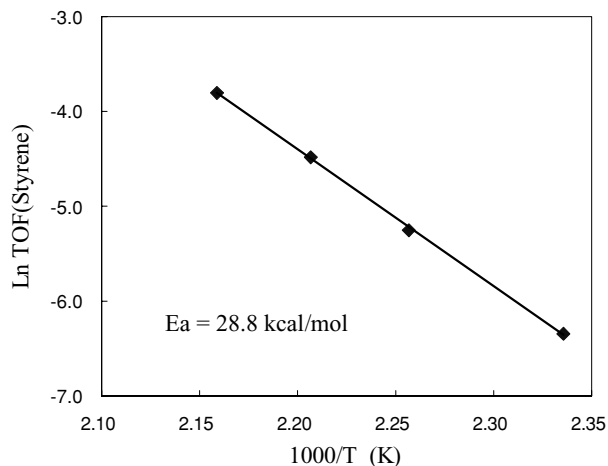

FIG. 1. The Arrehenius plot for styrene formation by oxidative arylation of ethylene with benzene catalyzed by Rh(ppy)$_2$(OAc). Conditions of temperature dependence: 190–155°C, 20 min.

is still unexplored. By the reaction with complex **1** at 180°C for 20 min, styrene was obtained (TOF = 113×10^{-4} s^{-1}; Table 1, entry 2), coupled with the formation of vinyl acetate (TOF = 34×10^{-4} s^{-1}). Although among these complexes the order of activities affected by leaving groups is Cl > acac > OAc, prominent differences regarding styrene formation were not observed. The reaction with **1** for 1 h resulted in production of styrene with almost the same TOF (109×10^{-4} s^{-1}; Table 1, entry 3) as that of the 20-min reaction. [Rh(bzq)$_2$Cl]$_2$ (bzq = benzo[h]quinoline–C^{10},N$'$) also gave styrene with a slightly larger TOF (165×10^{-4} s^{-1}; Table 1, entry 5) than that with [Rh(ppy)$_2$Cl]$_2$ (145×10^{-4} s^{-1}; Table 1, entry 1). Consistent with the smaller ν(Rh–Cl) frequency (32) (211 cm^{-1}) of [Rh(bzq)$_2$Cl]$_2$ than that of [Rh(ppy)$_2$Cl]$_2$ (233 cm^{-1}), bzq seems to be a slightly better translabilizing ligand than ppy. We also tested the activity of [RhCp*Cl$_2$]$_2$ (Cp* = η^5-pentamethylcyclopentadienyl). The complex demonstrated the styrene formation with a TOF approximately two times larger than that of [Rh(ppy)$_2$Cl]$_2$ at 180°C. RhCp*Cl(acac–O,O$'$) and [RhCp*(μ-acac–O,O$'$,C^3)]$_2$(BF$_4$)$_2$ showed activities similar to [RhCp*Cl$_2$]$_2$. Rh complexes having Cp* ligands as translabilizing groups were better catalysts than Rh complexes with ppy ligands. Rh(acac)(CO)$_2$, a Rh complex in a Rh(I) oxidation state at the beginning of the reaction, also led to the formation of styrene (TOF = 248×10^{-4} s^{-1}) and vinyl acetate (TOF = 83×10^{-4} s^{-1}; Table 1, entry 9) using O$_2$/Cu(OAc)$_2$ as oxidizing reagents.

To determine the activation parameters of oxidative arylation of ethylene with benzene catalyzed by **1** and [RhCp*Cl$_2$]$_2$ in the presence of O$_2$/Cu(OAc)$_2$, TOF for the production of styrene was measured at various temperatures. The TOF (styrene) by complex **1** increased from 0.0018 s^{-1} at 155°C to 0.0223 s^{-1} at 190°C. The Arrhenius plot of the reaction catalyzed by **1** is shown in Fig. 1.
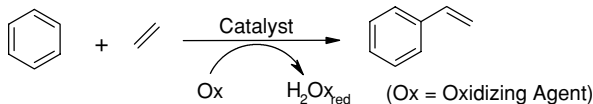
SCHEME 1

TABLE 1

Oxidative Arylation of Ethylene with Benzene to Produce Styrene [a]

Entry	Catalyst	mM	Oxidant	Additive[b]	Reaction time (min)	TN[c]		TOF[c] ($\times 10^{-4}$ s^{-1})	
						VA	Styrene	VA	Styrene
1	[Rh(ppy)$_2$Cl]$_2$	1.0	O$_2$/Cu(OAc)$_2$[d]	—	20	4.7	15.6	44	145
2	Rh(ppy)$_2$(OAc)	1.0	O$_2$/Cu(OAc)$_2$[d]	—	20	4.0	13.5	34	113
3	Rh(ppy)$_2$(OAc)	1.0	O$_2$/Cu(OAc)$_2$[d]	—	60	11.4	39.3	32	109
4	Rh(ppy)$_2$(acac)	1.0	O$_2$/Cu(OAc)$_2$[d]	—	20	4.9	14.9	45	138
5	[Rh(bzq)$_2$Cl]$_2$	1.0	O$_2$/Cu(OAc)$_2$[d]	—	20	5.5	17.9	51	165
6	[RhCp*Cl$_2$]$_2$	1.0	O$_2$/Cu(OAc)$_2$[d]	—	20	11.0	35.7	85	275
7	RhCp*(acac)Cl	1.0	O$_2$/Cu(OAc)$_2$[d]	—	20	13.0	31.6	120	293
8	[RhCp*(acac)]$_2$(BF$_4$)$_2$	1.0	O$_2$/Cu(OAc)$_2$[d]	—	20	11.5	28.1	107	260
9	Rh(acac)(CO)$_2$	1.0	O$_2$/Cu(OAc)$_2$[d]	—	20	10.0	29.8	83	248
10	[Rh(DPPB)(NBD)](BF$_4$)	0.8	O$_2$/Cu(OAc)$_2$[d]	—	20	4.1	4.1	34	34
11	Pd(OAc)$_2$	1.8	O$_2$/Cu(OAc)$_2$[d]	—	20	44	39	365	328
12	[Ir(ppy)$_2$Cl]$_2$	3.9	O$_2$/Cu(OAc)$_2$[d]	—	20	0.0	0.0	0	0
13	IrCp*(acac)Cl	3.3	O$_2$/Cu(OAc)$_2$[d]	—	20	5.3	0.5	15	1
14	IrCp*(acac)$_2$	3.0	O$_2$/Cu(OAc)$_2$[d]	—	20	5.2	2.0	15	6
15	[Ir(acac)$_3$]$_2$	0.8	O$_2$/Cu(OAc)$_2$[d]	—	20	4.8	4.4	45	40
16	Rh(ppy)$_2$(OAc)	1.0	O$_2$	—	20	0.0	1.5	0	13
17	[RhCp*Cl$_2$]$_2$	1.0	O$_2$	—	20	0.0	0.3	0	3
18	Rh(acac)(CO)$_2$	1.0	O$_2$	—	20	0.0	0.0	0	0
19	[Rh(DPPB)(NBD)](BF$_4$)	0.6	O$_2$	—	20	0.0	1.6	0	13
20	[Rh(ppy)$_2$Cl]$_2$	1.0	O$_2$	acacH	20	0.0	2.7	0	22
21	Rh(ppy)$_2$(OAc)	1.0	O$_2$	acacH	20	0.0	0.7	0	6
22	Rh(ppy)$_2$(acac)	1.0	O$_2$	acacH	20	0.0	2.0	0	19
23	[Rh(bzq)$_2$Cl]$_2$	1.0	O$_2$	acacH	20	0.0	3.0	0	28
24	[RhCp*Cl$_2$]$_2$	1.0	O$_2$	acacH	20	0.0	1.0	0	8
25	RhCp*(acac)Cl	1.0	O$_2$	acacH	20	0.0	1.0	0	10
26	[RhCp*(acac)]$_2$(BF$_4$)$_2$	1.0	O$_2$	acacH	20	0.0	5.1	0	47
27	Rh(acac)(CO)$_2$	1.0	O$_2$	acacH	20	0.0	22.5	0	188
28	[Rh(DPPB)(NBD)](BF$_4$)	0.8	O$_2$	acacH	20	0.0	21.6	0	180
29	Pd(OAc)$_2$	1.8	O$_2$	acacH	16	12	47	121	482
30	[Ir(acac)$_3$]$_2$	1.0	O$_2$	acacH	20	0	1	0	11
31	Rh(acac)(CO)$_2$	1.0	O$_2$	tmhd[e]	20	0.0	19.1	0	159
32	Rh(acac)(CO)$_2$	1.0	O$_2$	hfacacH[f]	20	0.0	0.5	0	4
33	Rh(acac)(CO)$_2$	1.0	O$_2$	aabe[g]	20	0.0	2.0	0	17

[a] Reactions proceeded at 180°C for 20 min in a benzene/acetic acid solution (10.6 M benzene).

[b] 670 mM additive was introduced.

[c] TN and TOF are based on Rh, Ir, or Pd.

[d] 50 mM Cu(OAc)$_2$ was added.

[e] 2,2,6,6-Tetramethyl-3,5-heptanedione.

[f] 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione.

[g] Acetoacetic acid tert-butylester.

The activation energy was 28.8 kcal/mol, obtained by the slope of the linear line. In comparison with this, the TOF (styrene) by [RhCp*Cl$_2$]$_2$ varied from 0.0088 s^{-1} at 150°C to 0.0275 s^{-1} at 180°C. The calculated activation energy obtained from the Arrhenius plot in Fig. 2 was 14.4 kcal/mol.

As a comparison, the reaction was also attempted with Pd(OAc)$_2$. Though the TOF for styrene formation was larger than that with the Rh complexes described above, vinyl acetate production was preferable to styrene formation by Pd(OAc)$_2$ (Table 1, entry 11). Although [Ir(ppy)$_2$Cl]$_2$, [IrCp*Cl$_2$]$_2$, IrCp*(acac–O,O′)Cl, and IrCp*(acac–O,O′)(acac–C^3), Ir complexes analogous to the Rh complexes used above, were also applied to the reaction, they did not produce styrene and vinyl acetate at all (Table 1, entries 12–14). [Ir(μ-acac–O,O′,C^3)(acac-O,O′)(acac–C^3)]$_2$, which is a very efficient catalyst for anti-Marcovnikov arylation (1) of olefin with benzene to produce alkylbenzene through CH bond activation of arene, showed very low activity for oxidative arylation of ethylene with benzene and, it is interesting to note, gave no ethylbenzene in this reaction media (Table 1, entry 15).

Entries 16–19 (Table 1) are the results of the reaction between benzene and ethylene carried out in the presence of O$_2$ without Cu(OAc)$_2$. Complex **1**, [RhCp*Cl$_2$]$_2$,
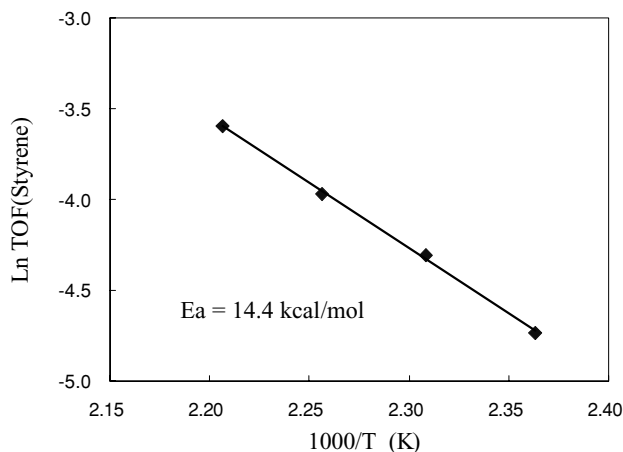
FIG. 2. The Arrehenius plot for styrene formation by oxidative arylation of ethylene with benzene catalyzed by $[Rh(Cp^*)Cl_2]_2$. Conditions of temperature dependence: 180–150°C, 20 min.

SCHEME 2

$Rh(acac)(CO)_2$, and $[Rh(NBD)(DPPB)]BF_4$ (NBD = bicyclo[2.2.1]hepta-2,5-diene, DPPB = 1,4-bis(diphenylphosphino)butane) showed poor activity for the reaction without $Cu(OAc)_2$. Generally, for the homogeneous oxidation reaction, an oxidizing agent such as Cu salt, Ag salt, or heteropoly acid is required in order to produce the catalytic reactions. That is, the oxidizing agent reoxidizes the group VIII metal complex reduced in the reaction, and then oxygen reoxidizes the oxidizing agent in reduced form. Accordingly, the oxidizing agent works as a cocatalyst.

However, in the presence of acacH and O_2 without $Cu(OAc)_2$, oxidative arylation of ethylene with benzene was catalyzed by $Rh(acac)(CO)_2$ to obtain styrene (TOF = 188×10^{-4} s^{-1}; (Table 1, entry 27). That is, the addition of acacH makes oxidative arylation directly forced by O_2 possible. Furthermore, in spite of the presence of acetic acid in the reaction medium, no formation of vinyl acetate was observed in the O_2/benzene/acetic acid/acacH system. [Rh
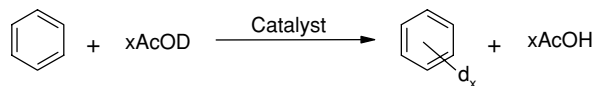
(NBD)(DPPB)]BF$_4$ also catalyzed oxidative arylation of ethylene to afford styrene (TOF = 180×10^{-4} s^{-1}; (Table 1, entry 28) and no vinyl acetate by addition of acacH and O_2. On the other hand, we also studied the reaction using various Rh(III) complexes in the presence of acacH and O_2. The rates with $[Rh(ppy)_2Cl]_2$, **1**, **2**, $[Rh(bzq)_2Cl]_2$, $[Rh(Cp^*)Cl_2]_2$, $RhCp^*Cl(acac–O,O')$, and $[RhCp^*(\mu\text{-}acac–O,O', C^3)]_2(BF_4)_2$ were almost one order of magnitude slower than those with Rh(I) complexes (Table 1, entries 20–26). Catalyzed by $Pd(OAc)_2$ in the presence of acacH and O_2, styrene was produced with smaller amounts of vinyl acetate (Table 1, entry 29) than in the presence of $O_2/Cu(OAc)_2$. However, in contrast to the reaction catalyzed by $Rh(acac)(CO)_2$, vinyl acetate was still afforded with $Pd(OAc)_2$. As a comparison study of additives, we introduced 2,2,6,6-tetramethyl-3,5-heptanedione, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, and acetoacetic acid *tert*-butylester into the reaction catalyzed by $Rh(acac)(CO)_2$ instead of acacH (Table 1, entries 31–33). 2,2,6,6-Tetramethyl-3,5-heptanedione and acacH showed much greater activity for this reaction than those which have electron-withdrawing groups.

3.2. Evidence for Arene CH Activation: H–D Exchange Reaction and Addition of PhHg(OAc)

To learn whether oxidative arylation involves C–H bond activation of benzene, we measured a H–D exchange (generally a good test for reversible CH bond activation) between C_6H_6 and CH_3CO_2D (6.0 M benzene) catalyzed by various Rh complexes in which benzene was activated through electrophillic substitution (Scheme 2). The results of the H–D exchange are given in Table 2. $[Rh(ppy)_2Cl]_2$ and complexes **1** and **2** were active for deuterium

TABLE 2

H–D Exchange Reaction between C_6H_6 and CH_3COOD[a]

Entry	Catalyst	mM	Oxidant	Additive	Temp (°C)	TN[b]	TOF[b] ($\times 10^{-3}$ s^{-1})
34	$[Rh(ppy)_2Cl]_2$	1.3	$O_2/Cu(OAc)_2$[c]	—	180	107	89
35	$Rh(ppy)_2(OAc)$	1.3	$O_2/Cu(OAc)_2$[c]	—	180	85	70
36	$Rh(ppy)_2(acac)$	1.2	$O_2/Cu(OAc)_2$[c]	—	180	117	98
37	$Rh(acac)(CO)_2$	1.7	—	—	160	0	0
38	$Rh(acac)(CO)_2$	1.7	O_2	—	160	0	0
39	$Rh(acac)(CO)_2$	1.7	O_2	acacH[d]	160	88	73

[a] Reactions proceeded for 20 min in a benzene/AcOD solution (6.0 M benzene).

[b] TN and TOF are based on Rh.

[c] 50 mM $Cu(OAc)_2$ was added.

[d] 670 mM acacH was introduced.

<div align="center">TABLE 3</div>

<div align="center">Oxidative Arylation of Ethylene with Benzene to Produce Styrene[a]</div>

Entry	Catalyst	mM	Additive/oxidant	TN[b]		TOF[b] ($\times 10^{-4}$ s^{-1})	
				VA	Styrene	VA	Styrene
40	RhCp*(acac)Cl	3.0	Cu(OAc)$_2$[c]	6.5	5.9	18	16
41	RhCp*(acac)Cl	2.7	PhHg(OAc)[d]	4.7	49.4	13	137
42	IrCp*(acac)Cl	1.3	Cu(OAc)$_2$[c]	0.0	0.0	0	0
43	IrCp*(acac)Cl	1.3	PhHg(OAc)[d]	0.0	0.0	0	0

[a] Reactions proceeded at 140°C for 60 min in a benzene/acetic acid solution (10.0 M benzene).

[b] TN and TOF are based on Rh or Ir.

[c] 500 mM Cu(OAc)$_2$ was added.

[d] 571 mM of PhHg(OAc) was introduced.

incorporation at 180°C (Table 2, entries 34–36). Regarding Rh(acac)(CO)$_2$, we examined the effect of the reaction environment in a H–D exchange. In contrast to the inactivity of Rh(acac)(CO)$_2$ without acacH (Table 2, entries 37 and 38), the combination of acacH and O$_2$ made Rh(acac)(CO)$_2$ active for deuterium incorporation at 160°C (Table 2, entry 39), which corresponds to the finding that the combination is available for styrene formation. Therefore, it is obvious that this catalysis proceeds through a C–H bond activation of benzene.

By addition of PhHg(OAc) to the reaction system, we should be able to skip the step of C–H bond activation of benzene and go directly to the next step, the Rh–Ph intermediate in the catalytic cycle. As shown in Table 3, the TOF for styrene formation at 140°C by RhCp*(acac)Cl using PhHg(OAc) was over eight times larger than that using benzene (Table 3, entries 40 and 41). Therefore, the rate-determining step of oxidative arylation of ethylene with benzene catalyzed by RhCp*(acac)Cl at 140°C appears to be CH activation of benzene. It is interesting that in spite of the addition of PhHg(OAc), IrCp*(acac)Cl was unable to form styrene (Table 3, entries 42 and 43).

Therefore, as can be seen in Scheme 3, we propose the following reaction mechanism: (i) CH bond activation of benzene by the Rh(III) center to produce a Rh-phenyl species, (ii) olefin insertion to produce a Rh–alkyl intermediate, (iii) product loss from the Rh center with β-hydride elimination, (iv) H$^+$ release by reductive elimination, and (v) reoxidation of the reduced Rh center.

3.3. Thermal Stability of the Rh Complex

As a test of thermal stability of Rh complexes in the reaction, a NMR study of complex **1**, as a representative for Rh complexes, was directed. ^{1}H NMR of **1** in AcOD at room temperature before heating is shown in Fig. 3A. ^{1}H NMR of the same solution after heating at 200°C under N$_2$ for 1 h is displayed in Fig. 3B. Free 2-phenylpyridine is not observed in Fig. 3B at all. Furthermore, compared to Fig. 3A, no change is observed except for a slight decrease in the H

signal at position (a) in Fig. 3B, which means that deuteration could occur at the position of C(11) in Fig. 4. By deuteration at C(11), ppy becomes a temporarily monodentate ligand coordinating through a N atom, which can rotate, and the C(7)–H(7) bond of ppy is activated by electrophilic substitution, followed by production of a new C(7)–Rh bond. At least in 1 h at 200°C, complex **1** is stable in the environment.

3.4. Synthesis and X-Ray Structure of **1** and **2**

Yellow crystals of complexes **1** and **2** were obtained, respectively, by the reaction of [Rh(ppy)$_2$Cl]$_2$ with KOAc and by the reaction of [Rh(ppy)$_2$Cl]$_2$ with Kacac. In order for the discussion above to be described, the full characterization of the structures of complexes **1** and **2** was required. We determined these crystal structures, which express molecular structures in a solid state, using single-crystal
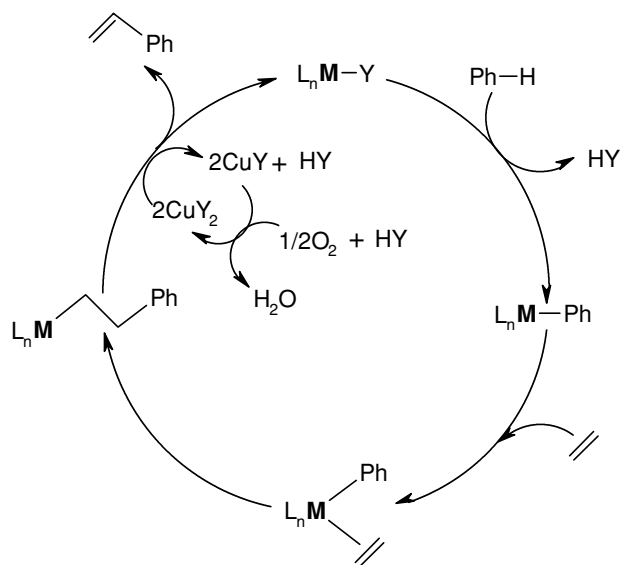
SCHEME 3. Proposed reaction mechanism for oxidative arylation of ethylene with benzene to produce styrene via CH bond activation, olefin insertion, and product loss, including redox system.
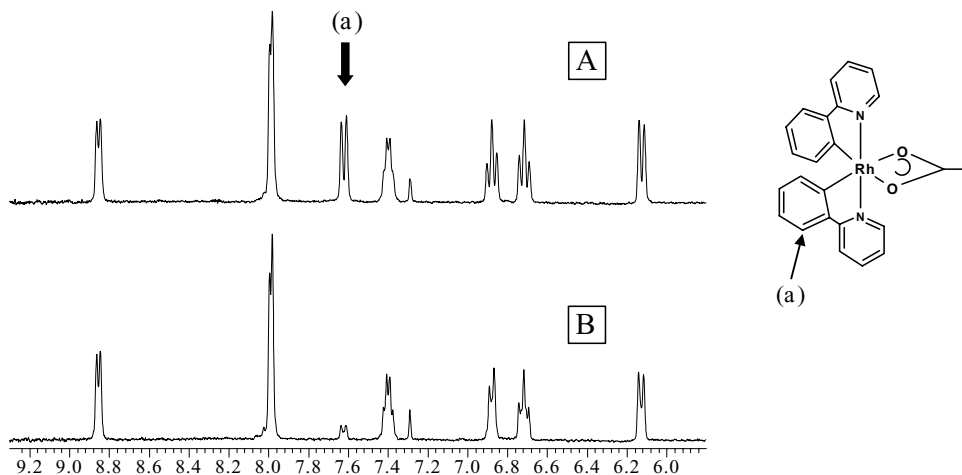
FIG. 3. ¹H NMR spectra of Rh(ppy)₂(OAc) in AcOD at room temperature as a test of thermal stability. (A) Before heating. (B) After heating at 200°C under N₂.

X-ray diffraction analysis. Results from NMR, giving information in a solution, from FD–MS, and from elemental analysis data are consistent with the determined structures.

The crystal data is shown in Table 4, and bond lengths and bond angles are shown in Tables 5 and 6. As can be seen in Fig. 4, complex **1** has two ppy ligands, which are crystallographically equivalent, and a bidentate OAc ligand. The structural determination confirms the *cis* arrangement of two cyclometalating carbon atoms in the ppy ligands. The complex shows a shorter Rh–C distance (1.966(4) Å) than the Rh–C distance (1.992(3) Å) of a similar compound, [Rh(ppy)₂(bpy)]PF₆ (33). Rh(III), Rh(II), and Rh(I) binuclear complexes having bridging OAc ligands and a Rh(I)

complex including monodentate OAc ligands are known, the Rh–O bond distances of which fall in the range 2.04–2.11 Å (34–38). In contrast to this, complex **1** has a significant, long Rh–O bond distance of 2.255(3) Å and this is the

FIG. 4. ORTEP drawing of Rh(ppy)₂(OAc) (**1**) determined by single-crystal X-ray analysis. Thermal ellipsoids are drawn at the 40% probability level.

TABLE 4

Crystal Data and Details of the Structure Determination for Complexes 1 and 2

Detail	1	2
Formula	$C_{24}H_{19}N_2O_2Rh$	$C_{27}H_{23}N_2O_2Rh$
Formula weight	470.33	510.40
Crystal System	Orthorhombic	Monoclinic
Space group	Aba2 (#41)	C2/c (#15)
Crystal color	Yellow	Yellow
a (Å)	11.154(2)	16.729(5)
b (Å)	14.748(3)	17.807(8)
c (Å)	12.059(2)	7.516(2)
α (deg)	90	90
β (deg)	90	99.01(2)
γ (deg)	90	90
V (Å³)	1983.8(5)	2211(1)
Z	4	4
D(calc) (g cm⁻³)	1.575	1.533
F(000)	952.00	1040.00
μ(MoKα) (cm⁻¹)	8.82	7.98
Crystal size (mm)	0.20 × 0.20 × 0.20	0.43 × 0.43 × 0.10
2θ range (deg)	6 < 2θ < 55	0 < 2θ < 70
Temperature (°C)	23.0	25.0
Radiation (Å)	0.71069 (Mo Kα)	0.71069 (Mo Kα)
No. of total data measured	2495	5553
No. of obsd unique data	2015(2σ)	4865 (3σ)
Residual electron density (e/Å³)	0.26	0.87
No. of params	132	146
R[a]	0.026	0.061
Rw[b]	0.029	0.115
TOF	1.22	1.11

[a] $R = \sum \|Fo\| - |Fc\| / \sum |Fo|$.
[b] $Rw = [\sum w(|Fo| - |Fc|)^2 / \sum w|Fo|^2]^{1/2}$.

TABLE 5

Major Bond Distances and Angles for Complex 1

Distances (Å)			
Rh–C(11)	1.966(4)	Rh–N(1)	2.026(2)
Rh–O(1)	2.255(3)	N(1)–C(1)	1.348(6)
N(1)–C(5)	1.357(5)	C(1)–C(2)	1.382(6)
C(2)–C(3)	1.369(6)	C(3)–C(4)	1.375(7)
C(4)–C(5)	1.393(5)	C(5)–C(6)	1.467(6)
C(6)–C(7)	1.387(5)	C(6)–C(11)	1.420(5)
C(7)–C(8)	1.395(6)	C(8)–C(9)	1.391(6)
C(9)–C(10)	1.399(5)	C(10)–C(11)	1.383(6)
O(1)–C(12)	1.264(4)	C(12)–C(13)	1.521(8)
Angles (deg)			
O(1)–Rh–O(1′)	58.5(2)	O(1)–Rh–N(1)	87.1(1)
O(1)–Rh–N(1′)	92.0(1)	O(1)–Rh–C(11)	108.1(1)
O(1)–Rh–C(11′)	165.6(1)	N(1)–Rh–N(1′)	178.9(3)
N(1)–Rh–C(11)	81.5(2)	N(1)–Rh–C(11′)	99.3(2)
C(11)–Rh–C(11′)	85.7(2)		
Torsion Angles (deg)			
N(1)–C(5)–C(6)–C(11)	−3.5(5)		

first example of a bidentate OAc ligand chelating to Rh(III) center.

The crystal structure of complex **2** is displayed in Fig. 5. Complex **2** is a Rh(III) complex analogous to complex **1**, which also has shorter Rh–C bond distance (1.973(2) Å) than the Rh–C bond of [Rh(ppy)₂(bpy)]PF₆. The Rh–O bond distance (2.172(2) Å) is also classified into the longest Rh–O bond (2.04–2.17 Å) of Rh complexes having acac ligands (39). Consequently, OAc and acac ligands seem to be easily removable ligands working as leaving groups in Rh–ppy complexes.

TABLE 6

Major Bond Distances and Angles for Complex 2

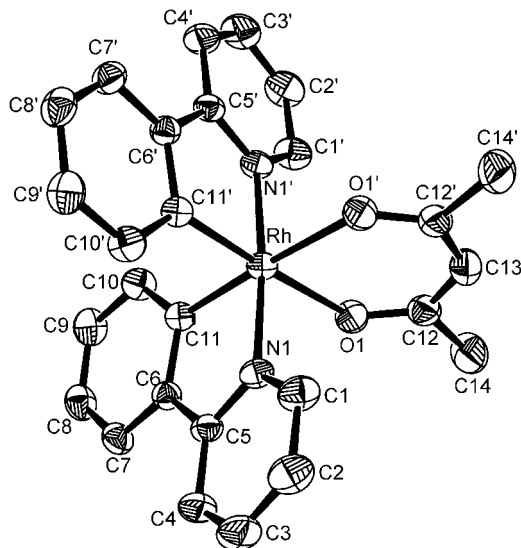| Distances (Å)			
Rh–C(11)	1.973(2)	Rh–N(1)	2.026(2)
Rh–O(1)	2.172(2)	N(1)–C(1)	1.347(3)
N(1)–C(5)	1.355(2)	C(1)–C(2)	1.387(4)
C(2)–C(3)	1.389(5)	C(3)–C(4)	1.384(4)
C(4)–C(5)	1.395(3)	C(5)–C(6)	1.463(2)
C(6)–C(7)	1.403(3)	C(6)–C(11)	1.405(2)
C(7)–C(8)	1.383(3)	C(8)–C(9)	1.392(4)
C(9)–C(10)	1.396(4)	C(10)–C(11)	1.404(3)
O(1)–C(12)	1.270(3)	C(12)–C(14)	1.516(5)
C(12)–C(13)	1.393(3)		
Angles (deg)			
O(1)–Rh–O(1′)	87.1(1)	O(1)–Rh–N(1)	88.00(7)
O(1)–Rh–N(1′)	95.81(7)	O(1)–Rh–C(11)	92.20(8)
O(1)–Rh–C(11′)	176.94(6)	N(1)–Rh–N(1′)	174.76(9)
N(1)–Rh–C(11)	81.20(7)	N(1)–Rh–C(11′)	95.03(7)
C(11)–Rh–C(11′)	88.7(1)		
Torsion Angles (deg)			
N(1)–C(5)–C(6)–C(11)	−3.9(2)		
O(1)–C(12)–C(13)–C(12′)	2.1(2)		

FIG. 5. ORTEP drawing of Rh(ppy)₂(acac) (**2**) determined by single-crystal X-ray analysis. Thermal ellipsoids are drawn at the 40% probability level.

4. CONCLUSIONS

We reported on the oxidative arylation of ethylene with benzene to produce styrene, that is, a one-step synthesis of styrene, catalyzed by a wide range of Rh complexes. Rh(III) complexes give a greater selectivity of styrene versus vinyl acetate than that with Pd(OAc)₂. Furthermore, Rh complexes in a Rh(I) oxidation state at the beginning of the reaction work as catalysts for the reaction without any oxidizing agent, such as Cu salt, by addition of acacH and O₂.

The mechanism of the reaction has not yet been fully elucidated but obviously involves CH activation of benzene by a Rh center to form a Rh-phenyl species, which appears to be a rate-determining step. The difference in translabilyzing groups comparatively affects the rate of the reaction in contrast to the minor effect made by changing leaving groups.

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